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EFFECT OF METALS ON THE OXIDATION RATE OF
RED PHOSPHORUS.

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OBJECT

To determine experimentally the effect of the common metals on the oxidation rate of red phosphorus both in the presence and absence of barium nitrate as a part of the project on non-corrosive priming compositions for small arms ammunition.

SUMMARY

In contact with various metals the oxidation rates of red phosphorous were found to be greatest with copper and least with aluminum as follows:

> copper > chromium#2 > bismuth > iron > silver > nickel
> cadmium > tin > red phosphorus alone > lead > chromium#1 > zinc
> duralumin > aluminum.

In contact with barium nitrate and various metals the oxidation rates of red phosphorous were found to be greatest with copper and least with aluminum as follows:

> copper > chromium#2 > bismuth > iron > silver > nickel
> cadmium > red phosphorus alone > chromium#1 > lead > tin > zinc
> duralumin > aluminum.

AUTHORIZATION

Frankford Arsenal Ordnance Laboratory Report No. 62A.

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I. INTRODUCTION

The initial work on red phosphorus came as a result of a search for a non-corrosive priming composition for small arms ammunition. The binary mixture red phosphorus-barium nitrate was finally selected(2) as the most promising.

However, primers prepared from this composition were found to show a serious lack of storage stability(2). The lack of stability has been attributed to the oxidation of the red phosphorus which produces various acids that cause the mixture to become insensitive after a few months.

Early in the investigation of the red phosphorus problem it was discovered that copper, 70:30 brass, and 90:10 brass were extremely active in accelerating the rate of oxidation of red phosphorus(1). Since it was known that red phosphorus oxidation resulted in poor stability of P4 Primer Compositions it was apparent that brass alone would not be satisfactory for the fabrication of primer cups and anvils.

At that time it was thought the problem might be solved by the use of brass, plated with some metal that was less reactive with red phosphorus. Several metals were tested for this purpose. They were nickel, tin, and cadmium, all of which were found to be less reactive than copper or brass. As a result, a storage program was conducted with nickel plated cups and anvils which increased the storage stability by approximately six months(2).

A study(1) was then made of the oxidation - reduction couples:

Metal - Metallic ion (of the common metals)
P - Hypophosphorous acid
Hypophosphorous acid - Phosphorous acid
Phosphorous acid - Phosphoric acid

From the study made the following conclusions were reached:

1. Mg^{++} , Al^{+++} , Zn^{++} , Cr^{+++} would not spontaneously oxidize red phosphorus, hypophosphorous acid, or phosphorous acid.

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- (1) Frankford Arsenal Ordnance Laboratory Report No. 62A
 - (2) Frankford Arsenal Ordnance Laboratory Report No. 80

2. It was possible for Cd^{++} or Fe^{++} to spontaneously oxidize hypophosphorous acid but not phosphorous acid or red phosphorus.

3. It was possible for Ni^{++} to spontaneously oxidize red phosphorus and hypophosphorous acid but not phosphorous acid.

4. It was possible for Sn^{++} , Pb^{++} , Fe^{+++} , Sn^{++++} , Cu^+ , Cu^{++} , and Ag^+ to spontaneously oxidize red phosphorus, hypophosphorous acid, and phosphorous acid.

With this background the experimental determination of the effect of the more common metals on the oxidation rate of red phosphorous as well as red phosphorus - barium nitrate mixtures was undertaken.

II. METHODS

Materials Used:

Red Phosphorus

Commercial Oldbury Amorphous Phosphorus which was given fifteen days preoxidation at 40°C and 90% R. H. after which the material was washed free of acids and vacuum dried.

Barium Nitrate

As required by U. S. Army Specifications No. 50-11-20A.

Metal Powders

Table I lists the analyses of the metals.

ANALYSES OF METAL POWDER

Metal	Mg	Al	Zn	Cr	Pb	Fe	Ni	Cu	Si	Ca
Magnesium	97.3	<.01	<.02	<.01	.01-.03	.05-.10	<.01	.01-.02	.01-.05	.005-.01
Aluminum	<.001	97.	---	---	---	.5-1.0	<.01	<.05	<.1	---
Duralumin	.5-.5	93.4	.1-.2	.03-.05	.01-.02	0.5	.02-.03	4.2	.5-1.0	---
Zinc	<.01	---	99.4	---	<.003	.01	---	.02	---	---
Cadmium	---	---	.05-.1	---	.1-.2	<.01	---	.01-.05	---	---
Phosphorus	---	.01-.05	---	---	.05-.10	.01-.05	<.01	.005	---	---
Chromium #1	<.01	9.4	.01-.02	87.8	---	1.63	.1-.2	.1-.2	.5-1.0	---
Copper	---	---	<.05	---	.1-.5	<.05	---	98.81	---	---
Iron	---	.025-.05	---	.05-.06	---	93.6	.03-.04	.08-.1	.30-.50	---
Nickel	---	.10-.50	---	<.01	---	.25	96.89	.16	<.05	---
Silver	---	---	.03-.05	---	<.01	.05	<.01	.01-.02	.1-.3	---
Tin	---	---	<.02	---	0.1	.02	---	.06-.08	---	---
Chromium #2	.01-.02	.74	---	94.1	.01-.02	1.06	.08	.13	.29	---

Metal

[illegible]

Mixtures A and B were prepared with each metal.

(5% metal powder
mixture A)95% red phosphorous

(75% barium nitrate
mixture B)25% mixture A

One gram samples of mixture A were prepared and stored in a cabinet maintained at 60°C and 90% R.H. and four gram samples of B were treated similarly. At various intervals samples were withdrawn and filtered, washed, and the filtrate plus washings were titrated with 0.1N sodium hydroxide to both methyl red and phenolphthalein end points.

The millimoles phosphorus acids both in the form of free acids as well as acid salts were then plotted against time.

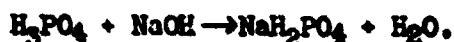
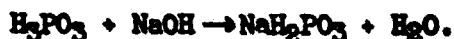
Calculation of millimoles of phosphorus acids from the two titrations:

10 (C-D) = millimoles phosphorus acids

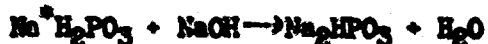
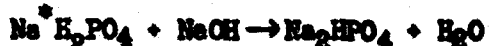
where C = ml 0.1N NaOH required for phenolphthalein end point.

D = ml 0.1N NaOH required for methyl red end point.

If all of the oxidized phosphorus consists of either phosphorus acid or phosphoric acid then $2D = C$ and at the methyl red end point the reactions



are completed. At the phenolphthalein end point the reactions:



are completed. In this case $10D$ or $10(C-D)$ or $5C$ is equivalent to millimoles of phosphorous acids.

* or other metal/valence

When the oxidized phosphorus present is in the form of phosphorous and phosphoric acids as well as their acid salts then 10D is equal to the millimoles of free acids present, and 10 (C-D) equals the millimoles of phosphorus acids both in the form of free acids as well as acid salts. It is evident that 5C does not equal the millimoles of phosphorus acids as it did in the first case.

III. RESULTS

Figures 1 and 2 illustrate the wide range of the effects of the metals on the oxidation rate.

The metals, with the exception of tin and cadmium can be grouped in three principal divisions which

- (1) Accelerate the oxidation greatly
- (2) Affect the oxidation slightly
- (3) Decrease the oxidation

The groups in the order of decreasing rates consist of:

Group I:

copper	iron
chromium#2	nickel
bismuth	silver

Group II:

lead	Chromium#1
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Group III:

zinc	duralumin
aluminum	

The tin and cadmium results were unusual. With red phosphorus alone tin accelerated the rate, but with red phosphorus plus barium nitrate tin decreased the rate considerably. Cadmium accelerated the rate sharply with red phosphorus alone but accelerated the rate only very slightly in the presence of barium nitrate.

The question of the effect of chromium on the rate remains unanswered in view of the high percentage of impurities present in both samples #1 and #2.

The data obtained as a result of this investigation fits into the framework of the oxidation-reduction potential calculations referred to in the introduction.

The decelerating effect of duralumin leads to the conclusion that the 4% copper present is not in a form which can ionize and thereby accelerate the phosphorus oxidation.

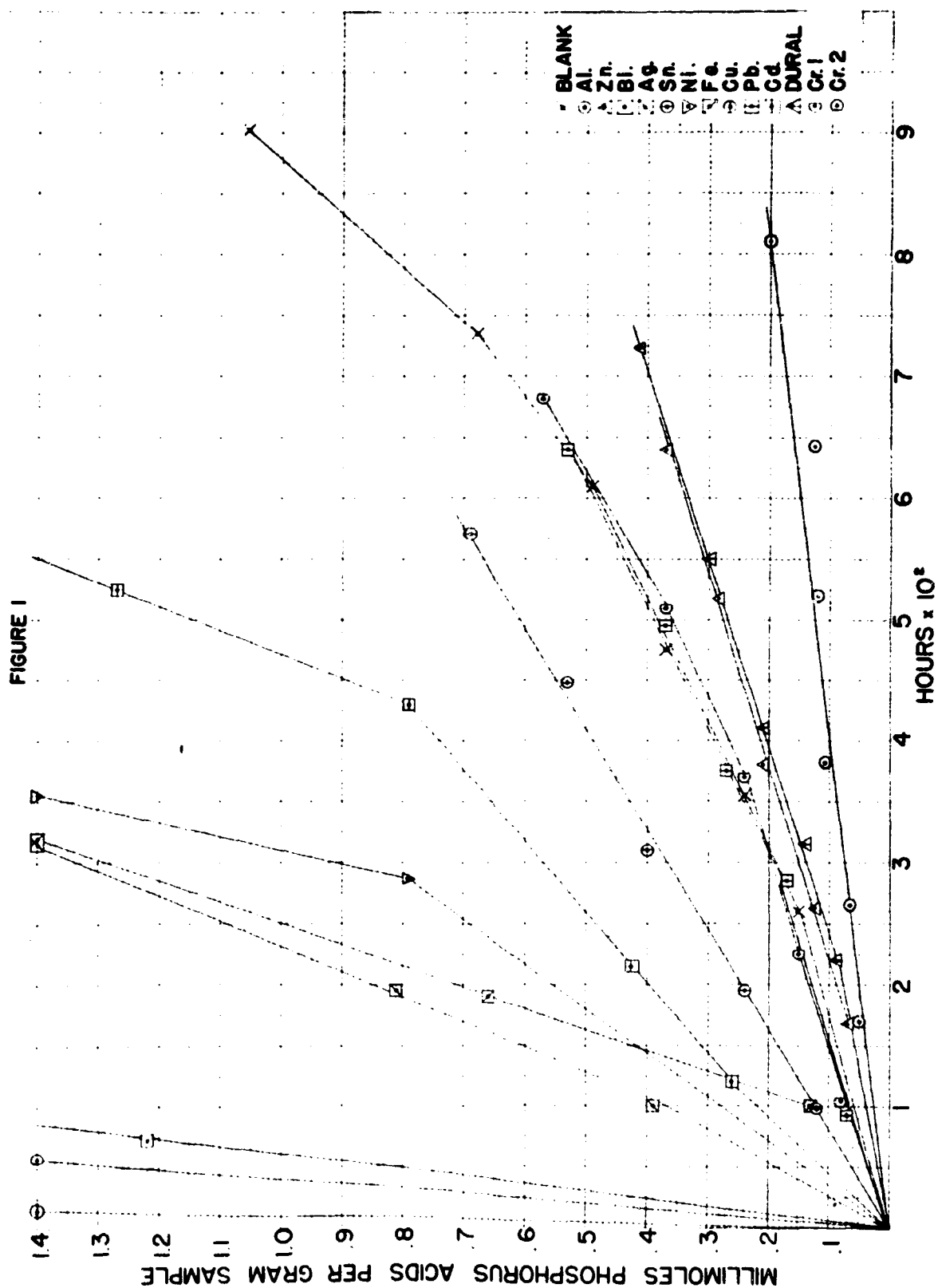
Retardation of the oxidation by aluminum, duralumin, and zinc, both in the presence and in the absence of barium nitrate, points to the choice of one of these as the metal that should be in contact with P4 primer composition in order to contribute to the greatest storage stability.

IV. CONCLUSIONS AND RECOMMENDATIONS

The effect of the metals investigated on the oxidation of red phosphorus varies over an extremely wide range. Hence the choice of the proper metal for contact with red phosphorus primer compositions is an important consideration in the storage stability of this type of primer.

The outstanding metal for this use appears to be aluminum and it is recommended that the use of this metal for primer cups and anvils be investigated.

EFFECT OF 5% METAL POWDERS ON THE OXIDATION RATE OF
RED PHOSPHORUS AT 60°C. AND 90% R. H.



MILLIMOLES OF PHOSPHORUS ACIDS PER FOUR GRAM SAMPLE

FIGURE 2

